DETERMINATION OF ALUMINIUM AS OXIDE

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I. INTRODUCTION

Although a considerable number of precipitants have been proposed for the determination of aluminium, direct precipitation of aluminium hydroxide by means of ammonium hydroxide, followed by ignition to oxide, is most commonly used, especially if no separation from iron is desired, in which latter case special methods must be employed. While the general principles involved in this determination are extremely simple, it has long been recognized that certain precautions in the precipitation, washing, and ignition are necessary if accurate results are to be obtained. While, however, most of these details have been studied and discussed by numerous authors, it is noteworthy that few publications or textbooks have taken account of all the factors. In the

present paper it seems desirable, therefore, to assemble the various recommendations and to consider their basis and their accuracy. No attempt has been made, however, to include a complete bibliography.

II. GENERAL PRINCIPLES

In precipitations of metallic hydroxides by means of ammonia or other bases the process may be considered as a progressive hydrolysis, brought about by the neutralization of the acid continuously set free. In the case of such hydroxides as ferric hydroxide, which are practically insoluble in bases, it may be readily shown that the solubility is decreased and precipitation rendered more complete by the addition of an excess of the precipitant, thereby increasing the hydroxyl ion concentration. However, in the case of amphoteric hydroxides, such as aluminium hydroxide, it is obvious that an excess of the base is to be avoided, and it therefore becomes desirable to select that degree of alkalinity which will insure most nearly complete precipitation and at the same time avoid resolution of the precipitate. As will be shown later, the study of the progress of the precipitation and the selection of the proper "end point" of precipitation can readily be accomplished by means of the hydrogen electrode, the conditions selected being subsequently defined by means of suitable indicators.

III. HISTORICAL

Early recognition of the fact that when considerable excess of ammonia is used in the precipitation of aluminium hydroxide appreciable amounts of aluminium pass into the filtrate, led to the time-honored procedure of boiling out most of the free ammonia. The latter method, however, has its defects, owing to the attack of glass vessels by the hot ammoniacal solution (leading to contamination of the precipitate with lime, silica, etc.); and to the possible re-solution of alumina, when through excessive boiling the solution becomes slightly acid. Various authors have therefore urged the use of a very slight excess of ammonia with only a short period of boiling,[1] especially when a considerable amount of ammonium chloride is present in the solution.[2] While the beneficial effect of ammonium chloride in reducing the solu-

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[1] S. L. Penfield and D. N. Harper, Amer. J. Sci., **32**, p. 107, 1886; Chem. News, **54**, pp. 90, 102, 1886; W. H. Daudt, J. Ind. Eng. Chem., **7**, p. 847, 1915.

[2] Malaguti and Durocher, Ann. Chim. Phys. (3), **17**, p. 421, 1846; J. Hanamann, Z. anal. Chem., **3**, p. 367, 1864; C. F. Cross, Chem. News, **39**, p. 161, 1879; L. Blum, Z. anal. Chem., **27**, p. 19, 1888; G. Lunge, Z. angew. Chem., p. 634, 1889.

bility of aluminium hydroxide in ammonia has been pointed out by numerous authors and has formed a basis for the procedures recommended in most textbooks, few attempts have been made to explain this effect, which in some cases has been attributed to the coagulation of the colloidal aluminium hydroxide by the salt.[3] While undoubtedly this is an important function of the ammonium chloride, it will be shown later that the reduction of the alkalinity (hydroxyl ion concentration) of ammonia by the presence of ammonium chloride also exerts a marked influence upon the amount of aluminium hydroxide held in solution.

Recognition of the errors attendant upon precipitation of aluminium with ammonia has led to the recommendation of other precipitants by means of which the maximum alkalinity of the solution is restricted; for example, ammonium sulphide, ammonium carbonate, sodium bicarbonate, ammonium nitrite, phenylhydrazine, and a mixture of potassium iodide and iodate. While for special cases—for example, the separation of aluminium from iron—one or more of the above methods may have special advantages, it may be shown that for general purposes their use is in no way preferable to that of ammonia under proper conditions, and that in most cases they present practical disadvantages.

While numerous authors recommend the customary method of using an indicator such as litmus paper to detect roughly the presence of an excess of ammonia, few, if any, have suggested the accurate definition of the desired alkalinity by means of suitable indicators. Hinrichsen used rosolic acid in a study of the effect of fluorine [4] upon the precipitation of aluminium hydroxide by ammonia, but gives no experimental or theoretical basis for its selection. Numerous authors, in efforts to develop methods for the volumetric determination of aluminium, or for testing the neutrality of aluminium salts, have used various indicators for determining the beginning and completion of the precipitation of aluminium hydroxide; but few, if any, have shown that complete precipitation actually occurs at the color change selected.

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[3] A. Classen, Quantitative Analysis, p. 145, sixth Ger. edition; 1912.

[4] Zts. anorg. Chem. 58: p. 88; 1908. In this paper Hinrichsen showed that fluorine may hinder or entirely prevent the precipitation of aluminium hydroxide by ammonia.

IV. PRECIPITATION OF ALUMINIUM HYDROXIDE

1. HYDROGEN ELECTRODE STUDIES

(a) THE METHOD.—The application of the hydrogen electrode to a study of the changes taking place in solution during precipitations was suggested in a paper on the determination of magnesia in limestone,[5] and was elaborated in an article by J. H. Hildebrand,[6] in which are given numerous curves for such precipitations, including the action of sodium hydoxide upon aluminium sulphate. The principle of the method is very simple, involving the measurement of the electromotive force of a cell consisting of a calomel half cell and a hydrogen electrode immersed in the solution to be investigated. The hydrogen ion concentration of the solution may then be calculated from the formula

$$\log \frac{1}{[H^+]} = \frac{\pi - 0.338}{0.058}$$

where π is the observed emf in volts at 25° C.

(b) APPARATUS AND SOLUTIONS EMPLOYED.—The apparatus and method of measurement were essentially those used by Hildebrand and Harned. The solution to be titrated was maintained at about 25° in a beaker which was closed with a rubber stopper having suitable perforations for (a) the hydrogen electrode, (b) the connection with a cell containing saturated potassium-chloride solution (used to eliminate the contact potential), which cell was in turn connected with a calomel half cell in 0.1 N potassium-chloride solution, (c) the tip of the burette, and (d) an exit tube for the hydrogen. By this arrangement carbon dioxide was conveniently expelled from the original solution by means of a current of hydrogen and was excluded during the titration. The emf readings were made at about 10-minute intervals by means of a millivoltmeter and capillary electrometer. The readings usually became constant to 1 or 2 millivolts within 20 minutes.

The aluminium-chloride solution, prepared from recrystallized aluminium chloride, was about decimolar (for $AlCl_3$) and contained a small amount of free hydrochloric acid. The sodium and potassium hydroxide solutions, prepared from the metals with exclusion of carbon dioxide, were about fifth normal. Fifth normal ammonium hydroxide was prepared by dilution of a sample of "C. P." ammonium hydroxide, furnished in a ceresin

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[5] J. H. Hildebrand and H. S. Harned, Orig. Com., Eighth Intern. Cong. Appl. Chem., 1, p. 217; 1912.
[6] Jour. Am. Chem. Soc., 35, p. 864; 1913.

bottle, and which by evaporation (of 100 cc) was found to contain a very small amount of organic matter, but no detectable amount of nonvolatile material.

(c) RESULTS OF HYDROGEN ELECTRODE EXPERIMENTS.—The data obtained by measurement of the changes in hydrogen ion
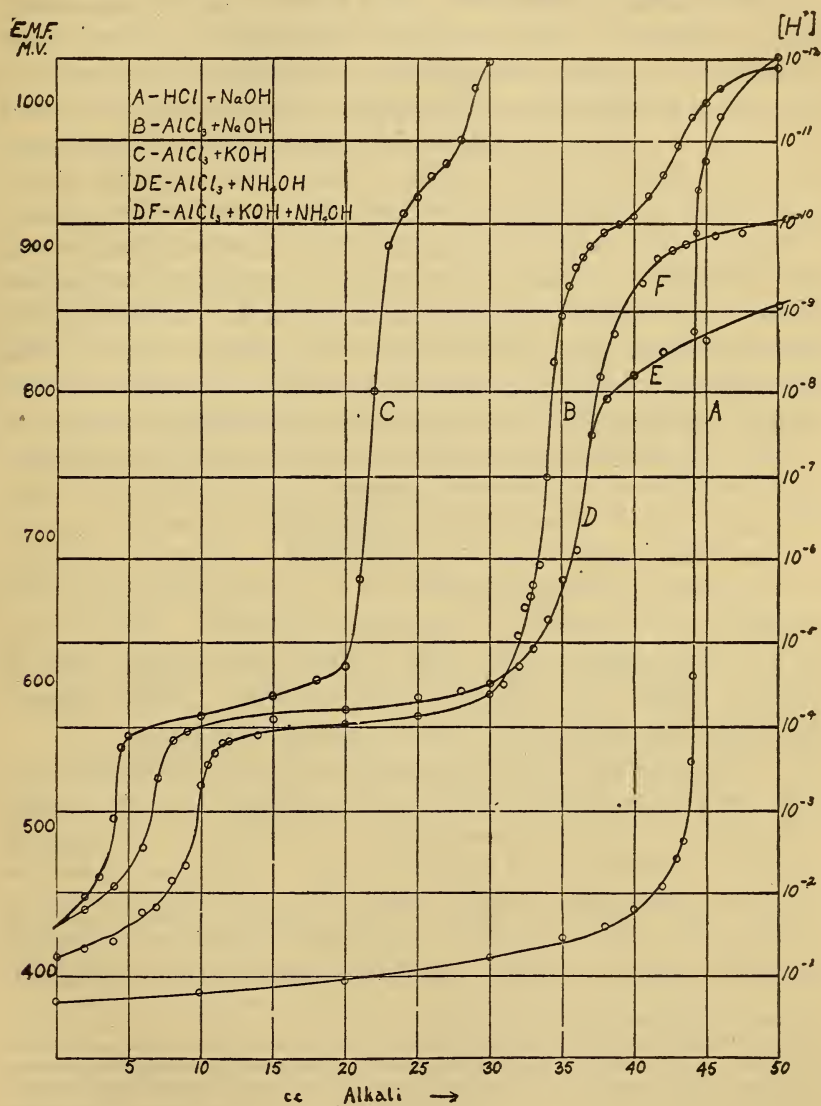

FIG. 1.—*Precipitation of aluminium hydroxide*

concentration occurring upon addition of alkaline hydroxides to solutions of aluminium chloride are shown graphically in Fig. 1. The abscissas represent cubic centimeters of alkaline hydroxide

added, and the ordinates on the left are the observed emf values expressed in millivolts. On the right side the value of the ordinates is expressed in terms of hydrogen ion concentration, calculated as previously stated. Curves *A*, *B*, and *C* are the same as were published in a preceding article by the author[7] on the constitution of aluminates. The curve *A* for the neutralization of hydrochloric acid with sodium hydroxide is shown simply to indicate the normal course of such a reaction in the absence of any metals precipitable as hydroxides. While curves *B* and *C* are chiefly of interest in relation to the formation of aluminates, they are included here in order to show the similarity in the course of the precipitations with fixed alkalies and with ammonia.

The curve *DE* shows the progress of the reaction when ammonium hydroxide is added to a solution of aluminium chloride containing a small amount of free acid. In order to eliminate the influence of ammonium chloride (to which reference will be made later) the curve *DF* was plotted, in which the portion *F* was obtained by the addition of ammonium hydroxide to a solution, in which the aluminium hydroxide had been exactly precipitated by the addition of a calculated amount of potassium hydroxide. While the curve *F* should strictly, therefore, be attached to curve *C'*, it has been placed in its present position in order to emphasize the comparsion between the effect of ammonium hydroxide with and without the presence of ammonium chloride. The curves *E* and *F* may contain slight errors arising from small losses of ammonia during the passage of the hydrogen. Their approximate shape and position is, however, clearly indicated.

(*d*) CONCLUSIONS FROM HYDROGEN ELECTRODE EXPERIMENTS.— From the curves shown in Fig. 1 it is evident that the changes taking place during the precipitation of aluminium chloride are practically independent of the alkali used. In general, it may be seen that precipitation[8] begins when $[H^+]$ is about 10^{-3} and is complete before $[H^+]$ is 10^{-7}. In the case of the fixed alkalies it was pointed out in a former paper that appreciable re-solution of

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[7] W. Blum, J. Am. Chem. Soc., **35**, p. 1499; 1913.

[8] By "precipitation" in this sense is meant the chemical formation of Al (OH)₃, which (especially in the absence of salts) may not actually coagulate or form a visible precipitate until from one-third to one-half of the alkali required for complete precipitation has been added. The point at which a visible precipitate occurred in the different experiments was found to be very variable. The formation of such regular curves as are shown, however, indicates the improbability of the existence in solution of any definite basic salts such as have been supposed to be formed by solution of freshly precipitated aluminium hydroxide in neutral aluminium chloride or sulphate solutions. Consult H. W. Fischer, Habilitationsschrift, Breslau, 1908, Chem. Zentr., I, p. 260, 1909; R. Kremann and K. Hüttinger, Jahr. K. K. Geol. Reichsan, **58**, p. 637, 1909 Chem. Zentr., II, p. 1200, 1909.

the precipitate, probably with the formation of aluminates, occurs soon after the neutral point is passed; for example, when [H$^+$] is less than 10^{-9}. When ammonium hydroxide is used as the precipitant, it may be seen from the curve *DE* that it is difficult to obtain a solution in which [H$^+$] is less than 10^{-9}, even when appreciable excess of ammonia is present. While, therefore, as is to be expected, it is not possible by this method to obtain complete solution in ammonia of any considerable quantity of aluminium hydroxide, an appreciable amount was always found dissolved [9] in any solutions in which [H$^+$] is less than 10^{-9}.

The effect of even small amounts of ammonium chloride in reducing the alkalinity of ammonium hydroxide is clearly shown by comparison of the curves *E* and *F*, there being present no ammonium chloride in *F*, and in *E* only the amount equivalent to about 37 cc of 0.2 *N* NH$_4$OH; that is, the solution at the end was about 0.08 *N* in NH$_4$Cl. This effect of ammonium chloride is also illustrated in Fig. 2, in which the hydrogen ion concentration of various ammonia-ammonium chloride solutions has been calculated from the ionization constant of ammonia at 25° [10]

$$\frac{[\text{NH}_4^+]\,[\text{OH}^-]}{[\text{NH}_4\text{OH}]} = 1.8 \times 10^{-5}$$

and that of water $K_w = 1.1 \times 10^{-14}$

upon the assumption that the mass law holds for such solutions. For the sake of simplicity the ionization of ammonium chloride, which in solutions from *N* to 0.1 *N* varies from 75 to 85 per cent [11] has been taken as 80 per cent. For convenience the results have been expressed in cc of *N* ammonium hydroxide present in a volume of 100 cc of ammonium-chloride solutions of various concentration.

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[9] *Existence of Ammonium Aluminate.*—In a previous communication the evidence in favor of the formation in solution of definite aluminates of sodium and potassium was presented. While no such definite evidence of the existence of ammonium aluminate is available, owing to the above-mentioned impossibility of securing ammonia solutions of high alkalinity, there seems to be no reason to doubt the analogy of the solutions in ammonia and the fixed alkalies. In this connection it is interesting to consider the evidence presented by C. Renz (Ber., **36**, III, p. 2751; 1903). This author dismisses the possibility of the existence of an ammonium aluminate, even though by an indirect method, viz, solution of Al(OH)$_3$ in Ba(OH)$_2$ and subsequent addition of (NH$_4$)$_2$SO$_4$, he was able to obtain a clear solution free from Ba^{++} and SO$_4^-$, 50 cc of which contained 0.1 g Al$_2$O$_3$. The fact, observed by Renz, that freshly precipitated Al(OH)$_3$ is readily soluble in organic amines, far from being an argument against the existence in solution, of ammonium aluminate, would appear to indicate that by the solution of aluminium hydroxide in any base aluminates are formed, the maximum concentration being dependent upon the alkalinity of the resultant solution and its consequent ability to repress the hydrolysis of the aluminate.

[10] A. A. Noyes and R. B. Sosman, Electrical conductivity of aqueous solutions, Carn. Inst. Pub., **63**, p. 228; 1908.

[11] F. W. G. Kohlrausch and L. Holborn, Leitvermögen der Elektrolyte, p. 159; 1898.

From Fig. 2 it is evident that (1) even small additions of ammonium chloride cause a marked decrease in the alkalinity of ammonium hydroxide solutions; (2) above 0.5 N an increase in the concentration of ammonium chloride has little effect; and (3) with any reasonable concentration of ammonium chloride, it is impracticable
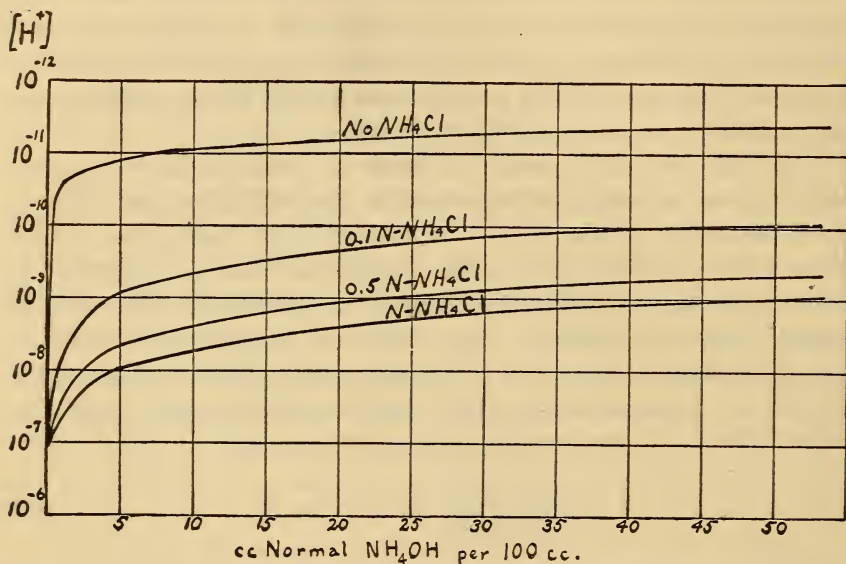

FIG. 2.—*Effect of ammonium chloride upon the alkalinity of ammonium hydroxide*

to so limit the alkalinity that a solution in which $[H^+]$ is less than 10^{-9} (that is, one which dissolves appreciable Al $(OH)_3$) is not formed when any large excess (for example, 5 cc) of concentrated ammonia is added. (It should be noted that 50 cc N NH_4OH about equals 3.3 cc conc. NH_4OH, sp. gr. 0.90.)

2. SELECTION OF AN INDICATOR FOR DEFINING THE CONDITIONS OF PRECIPITATION

If, as previously shown, precipitation of aluminum hydroxide by ammonia is complete before $[H^+]$ is 10^{-7}, and its re-solution is appreciable when $[H^+]$ is 10^{-9}, it is desirable to obtain some indicator which will change color when $[H^+]$ is about 10^{-7}. Experiments were therefore conducted with a few common indicators showing marked color changes near this point, viz, para-nitrophenol, methyl red, rosolic acid, and phenolphthalein. Litmus was not included because of its gradual color change. In each case the solution of the aluminium chloride and indicator contained in a platinum dish was heated just to boiling, and pure

ammonium hydroxide (about 2 N) was added carefully until the first definite color change occurred. The solution was then boiled for about two minutes to coagulate the precipitate and filtered into a platinum dish in which the filtrate was evaporated to dryness. After the careful expulsion of most of the ammonium salts, the residue in the dish was digested with concentrated hydrochloric acid and the solution and any undissolved residue were transferred to a weighed platinum crucible. After evaporation the residue was ignited and weighed. Correction was made for the residue obtained upon similar evaporation of the distilled water (about 0.0002 g for 200 cc) and for the nonvolatile matter contained in the added ammonium chloride (0.0002 g in 5 g). Since these corrections were of the same order of magnitude as most of the residues obtained, any of the latter less than 0.0002 g may be considered negligible. The results obtained are shown in Table 1.

TABLE 1

Precipitation of $Al(OH)_3$ by NH_4OH Using Various Indicators

[$AlCl_3$ solution equivalent to 0.10 g Al_2O_3, precipitated in a volume of 200 cc]

Experiment	Indicator	Color change [a] $[H^+]$=approximate	NH_4Cl added g	Al_2O_3 in filtrate g	Remarks
1	Para nitrophenol.................	10^{-6}	5	0.0010	
2	.....do.............................	10^{-6}	5	.0012	
3	Methyl red........................	$10^{-6.5}$	0	Appreciable.	Coagulated poorly.
4	.....do.............................	$10^{-6.5}$	5	.0001	
5	.....do.............................	$10^{-6.5}$	5	.0000	
6	Rosolic acid......................	$10^{-7.5}$	0	.0000	
7	.....do.............................	$10^{-7.5}$	5	.0000	
8	.....do.............................	$10^{-7.5}$	5	.0002	Macerated paper used.
9	Phenolphthalein.................	10^{-9}	0	.0004	
10	.....do.............................	10^{-9}	5	.0004	

[a] The approximate points of color change selected were measured with the hydrogen electrode at room temperature.

From Table 1 it is evident that considerable aluminium hydroxide remains unprecipitated when the solution is just alkaline to para-nitrophenol, while a smaller amount, but still appreciable, is redissolved when the solution is just alkaline to phenolphthalein. So far as accuracy is concerned, there is no choice between the use of methyl red and of rosolic acid. Practically, however, methyl red has been found preferable, because of its sharper color change, and because the end point is reached while approaching neutrality; that is, a slight excess of ammonia is less likely to

cause re-solution. Moreover, solutions just alkaline to methyl red are less likely to attack Jena or similar glassware than are solutions slightly alkaline to rosolic acid. In using methyl red, however, it is essential to have appreciable ammonium chloride present to facilitate coagulation. The fact that coagulation occurs more readily, even in the presence of only small amounts of ammonium chloride, when the solution is just alkaline to rosolic acid (that is, when $[H^+] < 10^{-7}$) would appear to indicate that the OH^- ion itself exerts a coagulating effect upon the colloid.

3. FACTORS AFFECTING THE FORM OF THE PRECIPITATE

Obviously, in actual analysis it is desirable not only to effect complete precipitation, but also to obtain the precipitate in a form that is readily filtered and easily washed. Such conditions are difficult to realize with a precipitated colloid, such as aluminium hydroxide. Numerous efforts have been made to devise conditions that will accomplish this end. In general, it has been recognized that while short boiling is desirable to effect coagulation, longer boiling renders the precipitate slimy and difficult to filter. As previously noted, the use of ammonium chloride is advantageous in producing the well-known salt effect in the coagulation of such a precipitate, as well as in reducing the actual solubility. These two factors were the only ones found to have a favorable influence upon the method of precipitation. The conclusion of W. E. Taylor,[12] that if the solution be heated to just 66° C before the addition of ammonia and subsequently boiled the precipitate is "granular," could not be confirmed by R. Sudgen [13] nor by the author. The recommendation of A. Guyard [14] to add glycerine to the solution before precipitating with ammonia was tried, and no improvement in the character of the precipitate was noted, while about 5 mg of Al_2O_3 were found in the filtrate. Similarly, the procedure of R. E. Divine,[15] viz, precipitation in the presence of tannic acid, while it produced an appreciable improvement in the character of the precipitate, yielded a filtrate containing from 1 to 5 mg of Al_2O_3, depending upon whether the solution was boiled for some time or was filtered after two minutes boiling.

While, therefore, it seems impossible to specify satisfactory conditions for the rapid filtration of considerable amounts of alu-

[12] Chem. News, **103**, p. 169; 1911.   [14] Z. anal. Chem., **22**, p. 426; 1883.
[13] Chem. News, **104**, p. 35; 1911.   [15] J. Soc. Chem. Ind., **24**, p. 11; 1905.

minium hydroxide, it is believed that for amounts up to 0.10 g Al_2O_3, the following conditions will yield fairly satisfactory results, viz: (1) The presence of at least 5 g of ammonium chloride in a volume of 200 cc; (2) addition of dilute ammonia to the nearly boiling solution until it is just alkaline to methyl red (or rosolic acid); (3) boiling for not more than two minutes; and (4) filtration without waiting long for the precipitate to subside. (In some cases the precipitate was found to settle quite readily; while in others it showed a tendency to rise to the surface and would not settle, even on long standing.) The addition of macerated filter paper before precipitation has been found advantageous in aiding filtration (and also ignition), especially of large amounts of the precipitate.

4. PRECIPITATION IN THE PRESENCE OF IRON

It is often necessary to precipitate ferric and aluminium hydroxides together. This can be accomplished readily by the procedure above recommended, since it was found that ferric hydroxide is completely precipitated by ammonia before the solution is alkaline to methyl red or to rosolic acid. In case sufficient iron is present to obscure the color of the indicator, it may be precipitated first by the careful addition of ammonia and caused to settle by short boiling, after which the color of the indicator can readily be recognized in the supernatant liquid and more ammonia added, if necessary, or any large excess of ammonia may be neutralized with dilute acid.

The writer has heard of an opinion (not published so far as known) that in the presence of ferric hydroxide the solubility of aluminium hydroxide in ammonia is decreased and that under such conditions there is less need for care in the addition of ammonia. Experiments have shown that this conclusion is unwarranted, since with any appreciable excess of ammonia considerable amounts of alumina were found in the filtrate even when large amounts of ferric hydroxide were present.

V. WASHING THE PRECIPITATE

In spite of the generally recognized fact that precipitates such as aluminium hydroxide readily assume the colloidal state when treated with pure water, many textbooks, even in recent editions, recommend the washing of aluminium hydroxide with hot water. That such a procedure is unsafe is readily seen from the fact that upon

washing precipitates equivalent to 0.10 g Al_2O_3, with only 75 cc of hot water, from 0.5 to 2 mg of Al_2O_3 were found in the washings. The obvious remedy, viz, washing with a solution of a volatile ammonium salt, such as ammonium chloride or nitrate, has been suggested by numerous authors.[16] From the standpoint of the "salt" action there appears to be no preference between ammonium nitrate and chloride. The former has been used most frequently, partly because of its slight advantage in assisting combustion of the filter paper and partly because of the opinion still prevalent, though frequently disproven, that the presence of ammonium chloride during ignition would cause loss of alumina by volatilization of the chloride.[17] As pointed out by W. F. Hillebrand,[18] when the original solution contains chlorides and it is desired to evaporate the filtrate and washings in platinum and to expel ammonium salts, it is undesirable to use ammonium nitrate in the wash water, owing to attack of the platinum vessels. In the present research, therefore, a hot 2 per cent solution of ammonium chloride was used. In view of the fact that, owing to hydrolysis, solutions of ammonium chloride and ammonium nitrate are slightly acid to methyl red, it was at first assumed that, as suggested by Trautmann,[19] there would be an advantage in rendering such solutions slightly alkaline with ammonia. In practice, however, it was found that there was no appreciable difference in the amount of alumina dissolved by the "neutral" and the alkaline solutions, the residues obtained from 100 cc of the washings being almost invariably less than 0.3 mg. The use of solutions of the pure salts, with no addition of ammonia, is therefore recommended, especially as solutions rendered alkaline are more likely to act upon the glass of the wash bottle and thus to become contaminated.

VI. SEPARATION FROM OTHER ELEMENTS

In the separation of aluminium from other elements of the succeeding groups in the usual analytical procedure by precipitation with ammonia, three sources of contamination may be encountered: (1) Adsorption of various compounds by the precipitate; (2) co-precipitation of hydroxides which require a con-

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[16] Penfield and Harper, Amer. J. Sci., 32, p. 107, 1886; W. Trautmann, Z. angew. Chem., 26 (aufsatz), p. 702, 1913; W. H. Daudt, J. Ind. Eng. Chem., 7, p. 847, 1915.

[17] It has been shown by Daudt (J. Ind. Eng. Chem., 7, p. 847, 1915) that 1 per cent ammonium chloride solution may be used for washing precipitates containing ferric hydroxide, with no loss of iron by volatilization.

[18] Bulletin 422, United States Geol. Survey, p. 99; 1910.

[19] Z. angew. Chem., 26 (aufsatz), p. 702; 1913.

siderable excess of ammonia for re-solution; and (3) formation of insoluble carbonates by absorption of carbon dioxide from the air.

The first effect is common, in some degree at least, to all the elements that may be present, the amount of a given element included in the precipitate being determined principally by its concentration in the solution, the character of the precipitate, and the method of washing. As previously pointed out, it has been found impracticable to precipitate aluminium hydroxide in any but a relatively gelatinous condition. It is obvious, therefore, that the only practical method of eliminating elements such as the alkalies, which are likely to be present in considerable amount in the solution, is to dissolve and reprecipitate. That such a procedure is quite efficient may be judged by the fact that from a solution containing 0.1000 g Al_2O_3 and 10 g of sodium chloride in a volume of 200 cc the precipitate obtained after a single precipitation and washing 10 times with 2 per cent ammonium chloride weighed 0.1071 g and contained much NaCl. A similar precipitate which was washed only 5 times, dissolved in hydrochloric acid, reprecipitated, and again washed 5 times weighed 0.1008 g and contained only a trace of NaCl.

The elements which introduce the second difficulty include zinc, manganese, nickel, and cobalt. It is well recognized [20] that the separation of aluminium from such elements by means of ammonia is unsatisfactory, since the alkalinity required for the resolution of their hydroxides is such as to cause appreciable solution of the aluminium hydroxide also. Moreover, it was found that even in solutions just alkaline to methyl red, oxidation and precipitation of manganese occurred so rapidly as to preclude a quantitative separation from aluminium. For such separations, therefore, other procedures—for example, the basic acetate method—must be employed.

The precipitation conditions above recommended have been found especially favorable in the separation from those elements such as barium, calcium, strontium, and, to a less extent, magnesium, whose carbonates are likely to be formed by absorption of carbon dioxide, and carried down by the precipitate. It has been found experimentally that in solutions containing barium and calcium, which are neutral or even slightly alkaline to rosolic acid—that is, $[H^+] = 10^{-7}$ to $10^{-7.5}$—it is impossible to form a

[20] A. A. Noyes, W. C. Bray, and E. B. Spear, J. Am. Chem. Soc., **30**, pp. 482 and 532; 1908.

precipitate of the carbonates by exposure to the atmosphere.[21] Aluminiumhydroxide precipitates obtained from solutions containing 0.1000 g Al_2O_3 and calcium and barium chlorides equivalent to 0.2 g CaO and BaO, respectively—that is, twice the amount of Al_2O_3—and washed 5 times with 2 per cent ammoniumchloride solution weighed 0.0998 and 0.0999 g, and were found to be free from calcium and barium.

The beneficial effect of ammonium chloride in the separation of aluminium from magnesium has long been recognized. Formerly it was explained by the formation of a double salt, though more recently it has been attributed to the repression by the ammonium chloride of the alkalinity of the ammonium hydroxide to a point insufficient to precipitate the magnesium hydroxide.[22] The latter view is confirmed by the results of Hildebrand and Harned,[23] who found that Mg (OH)$_2$ is not precipitated until [H$^+$] is less than 10^{-9}, and by the curves shown in Fig. 2 of this paper, in which the above effect of ammonium chloride is clearly shown. That the procedure recommended is effective in the separation of aluminium and magnesium is shown by experiments in which aluminium hydroxide equivalent to 0.10 g Al_2O_3, precipitated in the presence of magnesium chloride equivalent to 0.2 g MgO, contained less than 0.0010 g MgO.

VII. IGNITION AND WEIGHING OF THE PRECIPITATE

The principal questions involved in the ignition of the aluminium hydroxide are (1) the hygroscopicity of the ignited oxide; (2) the temperature and length of time required for dehydration; and (3) the effect of chlorides upon the ignition.

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[21] This observation is approximately in accordance with the result obtained by calculating the alkalinity of barium chloride or calcium chloride solutions—for example, o.1 N—saturated with respect to the neutral carbonates, in equilibrium with the normal atmosphere. (See J. Johnston, J. Am. Chem. Soc., **37**, p. 2001; 1915.) Thus the ionization of o.1 N barium-chloride solution may be assumed as 70 per cent: that is, [Ba^{++}] is o.07. Since at 16° the solubility product [Ba^{++}] [CO$_3^=$] equals 7×10^{-9}, the [CO$_3^=$] in such a solution is equal to 10^{-7}. In any solutions at 16° in equilibrium with an atmosphere containing CO$_2$ with a partial pressure P, $\dfrac{[OH^-]^2}{[CO_3^=]}$ i. e. $^2[OH^-]^2 = \dfrac{3.4 \times 10^{-11}}{P}$. While the ordinary atmosphere contains about three parts of CO$_2$ in 10 000, the air in a laboratory may often contain five parts or more in 10 000. In such a case $P = 5 \times 10^{-4}$, and therefore [OH$^-$]=o.84$\times 10^{-7}$. If $K_{w_{16}°} = 0.5 \times 10^{-14}$, then [H$^+$] is about 0.6×10^{-7} or $10^{-7.2}$; that is, the solution must be slightly alkaline before any BaCO$_3$ can be precipitated by exposure to air containing the normal amount of CO$_2$. From similar calculations for o.1 N CaCl$_2$, assuming that [Ca^{++}] [CO$_3^=$]=o.98$\times 10^{-8}$, it may be shown that [OH$^-$]=1.0$\times 10^{-7}$; or [H$^+$]=o.5$\times 10^{-7}$ or $10^{-7.3}$ before any CaCO$_3$ will be precipitated upon exposure to the atmosphere. Moreover, such carbonates are prone to form supersaturated solutions and precipitation may not occur even at the points designated.

[22] J. M. Loven, Z. anorg. Chem., **11**, p. 404, 1896; F. P. Treadwell, Z. anorg. Chem., **37**, p. 326, 1903; W. Herz and G. Muhs, Z. anorg. Chem., **38**, p. 138, 1904.

[23] Orig. com., Eighth intern. cong. Appl. Chem., **1**, p. 217; 1912.

1. HYGROSCOPICITY OF ALUMINIUM OXIDE

The fact that ignited Al_2O_3 readily absorbs water has been recognized and pointed out by many authors.[24] This property has, in fact, been made the basis for the recommendation of the use of Al_2O_3 as a dehydrating agent.[25] It should be noted, however, that for the latter use the Al_2O_3 should not be strongly ignited. Many of the experiments that have been conducted to determine the hygroscopicity of such substances as Al_2O_3 have little bearing upon analytical procedures, since no distinction was made between the amount of water absorbed and the rate of absorption, especially during the first few minutes exposure. Tests at this Bureau have shown that in common with most substances capable of absorbing moisture (even those not intrinsically hygroscopic) recently ignited Al_2O_3 absorbs within the first 10 minutes exposure to the atmosphere a large proportion of the water which it will absorb in 24 hours. Since, as frequently pointed out, the atmosphere in an ordinary desiccator which has recently been opened is not greatly different from the atmosphere prevailing in the room, it is obvious that the all too common practice of placing in a desiccator ignited precipitates such as Al_2O_3 in uncovered crucibles, is likely to lead to even greater errors than those resulting during the period required for rapid weighing. That a well-fitting cover on a platinum crucible is efficient in preventing absorption of moisture in the desiccator or on the balance has been frequently demonstrated. Thus, a crucible containing 0.10 g ignited Al_2O_3, which when allowed to stand covered upon the balance showed no appreciable change in weight in five minutes, gained as much as 0.0010 g when uncovered for five minutes. For any accurate work in the determination of alumina, therefore, and especially in any experiments designed to test the temperature and period required for the ignition of such substances, it is absolutely essential that the crucible be well covered both in the desiccator and upon the balance.

2. TEMPERATURE AND TIME OF IGNITION

Directions for the ignition of alumina [26] have usually prescribed blasting for periods varying from 10 to 30 minutes, followed by successive short periods until constant weight is secured. While it is evident that in order to expel the last traces of moisture from

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[24] C. F. Cross, Chem. News, **39**, p. 161, 1879; Hess and Campbell, J. Am. Chem. Soc., **21**, p. 776, 1899; E. T. Allen and V. H. Gottschalk, Am. Chem. Jour., **24**, p. 292, 1900.

[25] F. M. G. Johnson, J. Am. Chem. Soc., **34**, p. 911; 1912.

[26] H. Moissan, Compt. rend., **121**, p. 851, 1895; P. H. Walker and J. B. Wilson, Chem. Eng., **16**, p. 159, 1912; W. H. Daudt, J. Ind. Eng. Chem., **7**, p. 847, 1915; and numerous textbooks.

such a precipitate, originally in a gelatinous condition, the use of a high temperature is desirable, it may be readily shown that long blasting is not necessary, at least for precipitates up to 0.2 g Al_2O_3. In numerous experiments with 0.1 g Al_2O_3 the total loss in weight produced by various periods of blasting following the first 5 minutes blasting was less than 0.0002 g. In order to show conclusively that dehydration is complete after 5 or 10 minutes blasting, at a temperature from 1100° to 1150° C, a covered crucible, of especially pure platinum, containing 0.7 g Al_2O_3, derived from three precipitates each of which had been blasted for 5 minutes, was again blasted for 5 minutes and placed in a vacuum sulphuric acid desiccator, which was quickly exhausted. After cooling, the crucible was quickly weighed against a tared crucible, and was then heated for three periods of 10 minutes each to a temperature of 1440° to 1460° in an electric furnace.[27]

The results of the experiments were as follows:

TABLE 2

Ignition of Al_2O_3

	Weight against tare
	Grams
Empty crucible..	3.1665
Including Al₂O₃ (previously blasted but exposed in transfer)...............................	3.8953
After five minutes blasting..	3.8943
Weight of Al₂O₃..	0.7278
After 10 minutes at 1440°–1460°...	3.8943
After second 10 minutes at 1440°–1460°...	3.8941
After third 10 minutes at 1440°–1460°...	3.8940
Weight of empty crucible after brushing out precipitate...................................	3.1662
Weight of Al₂O₃ after heating..	0.7278

From these results it is evident that, making allowance for the loss in weight of the platinum crucible (0.0003 g), exposure to a temperature of over 1400° C produced no appreciable change in weight of Al_2O_3 previously blasted for not over 15 minutes.

From these results it is apparent that the continued losses in weight noted by some authors upon successive blastings of Al_2O_3 were probably due, not to further dehydration of the precipitate, but to losses in weight of the crucibles (which in commercial

platinum may be quite appreciable); or, in case the crucibles were not covered while in the desiccator and on the balance, to a decrease in the hygroscopicity of the precipitate. In other words, at no time was the true anhydrous weight obtained, but always a weight including some amount of absorbed moisture, which amount decreases (and may become almost negligible) after the precipitate has been heated to high temperatures for a considerable period. Owing to the frequent failure to mention whether the crucibles were covered during the ignition and weighing, it is impossible to determine in which cases the above criticism applies. Such omissions indicate, however, a lack of appreciation of the importance of covering the crucibles.

3. EFFECT OF AMMONIUM CHLORIDE UPON THE IGNITION

The still prevalent misconception that when aluminium hydroxide containing ammonium chloride is ignited, there is loss of aluminium, dates back at least to 1875.[28] It has been disproven so frequently [29] that it would be superfluous to dwell upon it were it not for the fact that it is referred to even in recent textbooks. The following experiments, while not essential to establish this, are perhaps of interest in still further demonstrating the absence of such an effect. Measured portions of a pure $AlCl_3$ solution were evaporated to small volumes in weighed platinum crucibles, after which pure ammonia in slight excess was added. Evaporation was continued to dryness and the residues were heated until all ammonium salts were expelled, and were finally blasted and weighed. The results, together with those obtained by the procedure recommended below (which had been found to give accurate results with metallic aluminium) are shown in Table 3.

TABLE 3

Experiment	Method	50 cc $AlCl_3$ yielded Al_2O_3
		Gram
1	Direct evaporation	0.0998
2	.....do	.0997
3	Precipitation	.1002
4	.....do	.1001
5	.....do	.1000
6	.....do	.0999

[28] C. R. Fresenius, Quantitative analysis, sixth Ger. edition; 1875.
[29] Allen and Gottschalk, Am. Chem. Jour., 24, p. 292, 1900; W. F. Hillebrand, Bull. 422, United States Geol. Survey, p. 99, 1910; W. H. Daudt, J. Ind. Eng. Chem., 7, p. 847, 1915.

From Table 3 it may be seen that in experiments 1 and 2, where the aluminium hydroxide was certainly in very intimate contact with an excess of ammonium chloride, any loss of aluminium by volatilization was so small as to be negligible. Moreover, the weights in experiments 3–6 include corrections for the filter ash and for known small impurities in the reagents and water, and are therefore probably somewhat less accurate than those obtained by direct evaporation.

VIII. PROCEDURE RECOMMENDED

From the foregoing considerations the following conditions are recommended for the determination of aluminium hydroxide. To the solution containing 5 g of ammonium chloride per 200 cc of solution, or an equivalent amount of hydrochloric acid, add a few drops of methyl red (0.2 per cent alcoholic solution) and heat just to boiling. Carefully add dilute ammonium hydroxide dropwise until the color of the solution changes to a distinct yellow. Boil the solution for one to two minutes and filter at once. Wash the precipitate thoroughly with hot 2 per cent ammonium chloride (or nitrate) solution. Ignite in a platinum crucible and after the carbon is all burned off blast for five minutes; cover the crucible and place it in a desiccator until cool. Weigh covered as rapidly as possible. A second blasting of five minutes is desirable, especially as it permits a more rapid weighing, and consequently probably more accurate results.

IX. CONFIRMATORY EXPERIMENTS

A weakness of many of the published researches upon the determination of aluminium is the lack of suitable standards by which to test the proposed methods. The use for this purpose of hydrated salts of possibly uncertain hydration, such as the alums, is not to be recommended for accurate work, and in the few cases where metallic aluminium has been used no detailed evidence of the purity has been presented. The following few experiments, though by no means exhaustive, appear to show that the method just described will yield results accurate to at least 1 part in 300 (which is more than sufficient for most purposes), and probably better.

Two samples of the purest aluminium that could be obtained in 1912 from the Aluminum Company of America were analyzed

by the methods described by J. O. Handy,[30] yielding the following results for the only elements that could be detected,

TABLE 4

Analysis of Aluminium

Sample	A	B
	Per cent	Per cent
Silicon	0.13	0.16
Copper	.01	.01
Iron	.25	.17
Aluminium (difference)	99.61	99.66

Weighed portions (about 1.3 g) of these samples were dissolved in hydrochloric acid and the solutions were oxidized with a small amount of nitric acid and filtered to remove silicon. The filtrates were diluted to measured volumes and aliquots used for the determination of aluminium as above described, about 0.25 g of Al_2O_3 being weighed in each determination. The ammonia was redistilled and all reagents carefully tested and found free from appreciable contamination. The weights of precipitates were corrected for the filter ash and for the amount of Fe_2O_3 corresponding to the iron found by the previous analysis. The results are shown in Table 5.[31]

TABLE 5

Aluminium Determination in Metallic Aluminium

Experiment	Sample	Weight of sample	Found		Al	
			Al_2O_3	Al	Found	By difference
			g	g	Per cent	Per cent
1	A	0.1298	0.2445	0.1297	99.90	99.61
2	A	.1298	.2443	.1296	99.82	99.61
3	B	.1288	.2428	.1288	99.95	99.66

[30] J. Am. Chem. Soc., 18, p. 768; 1896.

[31] In calculating the weight of aluminium present in the Al_2O_3, the 1916 atomic weight of Al=27.1 has been used. It is at least interesting, though probably not significant with so few experiments, to note that if the round atomic weight 27 be used for Al the values for per cent Al found become, respectively, 99.73 and 99.67 for A and 99.78 for B—that is, they approach the amount found by difference, well within the experimental limit. No probable source of error in the determinations in Table 5 is likely to account for the existing discrepancies, amounting to from 0.0006 to 0.0008 g Al_2O_3. More experiments are required to throw light upon these discrepancies. The point is merely mentioned as of interest in connection with the statement of F. W. Clarke (Recalculation of the Atomic Weights, p. 268, 3d edition, 1910), that "the atomic weight of aluminium needs reinvestigation."

X. CONCLUSIONS

From the above experiments the following conclusions may be drawn, many of which simply confirm those of previous investigators:

(1) From observations made with a hydrogen electrode and with suitable indicators it was found that the precipitation of aluminium hydroxide by ammonium hydroxide is complete when $[H^+]$ is between $10^{-6.5}$ and $10^{-7.5}$, points approximately defined by the color change of methyl red and of rosolic acid.

(2) The presence of ammonium chloride during precipitation is advantageous in limiting the alkalinity and in coagulating the precipitate.

(3) Solutions of ammonium nitrate and chloride are equally satisfactory for washing the precipitate.

(4) The conditions of precipitation recommended are favorable for the simultaneous precipitation of aluminium and ferric hydroxides; and for their separation from calcium, strontium, barium, and magnesium.

(5) Crucibles containing ignited alumina should be kept covered in the desiccator and on the balance.

(6) For precipitates of from 0.1 to 0.2 g Al_2O_3 5 or 10 minutes blasting is sufficient.

(7) The presence of ammonium chloride during ignition causes no appreciable loss of alumina.

WASHINGTON, March 31, 1916.